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Final Report 6322-4, Phase II
Covering the Period 1 November 1977 to 31 May 1978

DEGRADABLE BINDERS FOR ORDNANCE DISPOSAL

By: D. G. Hendry, G. E. Manser, R. A. Kenley,
and D. L. Ross

Prepared for:

NAVAL SURFACE WEAPONS CENTER
White Oak Laboratory
Silver Spring, MD 20910

Attention: Code WR-15

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The objectives of the current program are to prepare one or more candidate plastic bonded explosives (PBX) that will undergo controlled, thermal degradation to a processable material to provide the Navy with a degradable PBX for interim qualification. Under previous contracts, difunctional (OH) azo compounds incorporated into polyurethane binders provided a degradable PBX loaded with HMX. Under phase I of the current program we prepared a difunctional azo compound (the degradable binder unit) that can be used for RDX-loaded PBXs. In Phase II, we

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have formulated and tested PBXs containing optimum degradable units developed in Phase I.

A thermally sensitive binder system has been developed for use in plastic bonded explosive (PBX) containing RDX filler. The thermally sensitive component in the formulations is the azo compound 1,1'-bis(3-hydroxypropyl)1,1,1',1'-tetraisobutyl azomethane (BPTA). This structure was selected based on its decomposition kinetics and ease of preparation. Because the compound is a primary diol, it is readily incorporated into crosslinked polyurethane binder formulations. The kinetic data indicate the binder has long-term stability with little change of physical properties at ambient conditions. However, when heated at 140°C (for approximately 1 hr), the binder degrades from a resilient insoluble material to a viscous fluid that is readily soluble.

Good compatibility was observed between BPTA and all ingredients. Differential scanning calorimetry of the PBX gave an onset of endotherm and exotherm only 3 and 4°C, respectively, below that of pure RDX. Vacuum thermal stability of the PBX at 100°C for 48 hr gave less than 1 cc/g of gas, which was comparable to pure RDX and well below the acceptable limit of 2 cc/g.

These results are extremely encouraging, and we recommend that further development and testing be carried out on a larger scale to obtain interim qualification of the most promising formulation. In general, we believe that BPTA can be incorporated into a wide variety of polyurethane formulations using polyether diols to generate a heat-sensitive polymer decomposing at 140°C.

SRI International

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Approved:

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PREFACE

The work described in this report was performed by SRI International under Contract No. N60921-77-C-0095, for Naval Sea Systems Command. The report summarizes research performed during the period 1 November 1977 to 31 May 1978. The work was done by the Physical Organic and Organic Chemistry Groups of the Chemistry Laboratory, Physical Sciences Division, with support from the Polymer Sciences Group in the same Laboratory.

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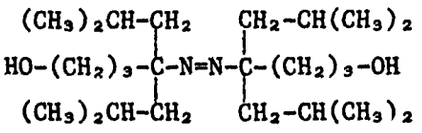
SUMMARY AND CONCLUSIONS

A thermally sensitive binder system has been developed for use in plastic bonded explosive (PBX) containing RDX filler. The thermally sensitive component in the formulations is the azo compound 1,1-bis(3-hydroxypropyl)-1,1,1',1'-tetraisobutyl azomethane (BPTA).



BPTA

This structure was selected because of its favorable decomposition kinetics and ease of preparation. Because the compound is a primary diol, it is readily incorporated into crosslinked polyurethane binder formulations. The kinetic data indicate the binder has long-term stability with little change of physical properties at ambient conditions. However, when heated at 140°C (for approximately 1 hr), the binder degrades from a resilient insoluble material to a viscous fluid that is readily soluble in common organic solvents.

A formulation composed of BASF Wyandotte's polyglycol L-35 and TPE-4542, Dupont's diisocyanate Hylene W, and BPTA was loaded to the extent of 80 wt %, with RDX having a trimodal particle distribution on a 10-g scale. The PBX was unaffected by agitating in methylene chloride, but after it was heated at 140°C for 1 hr, the RDX could be recovered by washing with the same solvent.

Good compatibility was observed between BPTA and all ingredients. Differential scanning calorimetry of the PBX gave an onset of endotherm and exotherm only 3 and 4°C, respectively, below that of pure RDX. Vacuum thermal stability of the PBX at 100°C for 48 hr gave less than 1 cc/g of gas, which was comparable to pure RDX and well below the acceptable limit of 2 cc/g.

We investigated the conditions for maximum molecular weight reduction with the minimum amount of BPTA. Results indicated that the ratio of [BPTA]/[crosslinks] should be at least 0.5 to allow conversion of insoluble crosslinked polymer to a soluble linear polymer upon total decomposition of the BPTA. Because further degradation is desired to reduce the molecular weight further, a [BPTA]/[crosslink] ratio of 1.0 is preferred. In this case the binder will become soluble in the time required to decompose one-half of the BPTA. Total decomposition of BPTA reduces the molecular weight to that approximately equal to the molecular weight per crosslink of the original polymer. Larger ratios of [BPTA]/[crosslink] cause faster degradation of properties under identical concentrations but do not significantly reduce the final molecular weight beyond the values obtained with a ratio of unity.

These results are extremely encouraging and we recommend that further development and testing be carried out on a larger scale to obtain interim qualification of the most promising formulation. In general, we believe that BPTA can be incorporated into a wide variety of polyurethane formulations using polyether diols to generate a heat-sensitive polymer decomposing at 140°C. Work must still be performed to determine if BPTA can be used in binder formulations containing hydroxy-terminated or carboxy-terminated polybutadiene.

INTRODUCTION

Objective

The objective of this program is to provide the Navy with one or more new PBXs that can be purposely and readily degraded at any time after manufacture and safely removed from casings for recylce or disposal of ingredients. Under previous contracts, we demonstrated that the basic concept of a thermally degradable PBX is feasible. A heat-sensitive binder containing azobisisobutanol was prepared and loaded to 80 wt% with HMX having a bimodal particle distribution.[1] Testing of the PBX (ABIB-PBX-2) showed no evidence that the heat-sensitive group affected its general stability. Vacuum thermal stability tests at 100°C gave barely detectable amounts of gas (<0.01 cm^3/g). Drop weight sensitivity indicated a 2.6-fold reduction in sensitivity, compared with pure HMX. Differential scanning calorimetry (DSC) indicated an exotherm at about 240°C, consistent with other PBXs containing HMX. The HMX was quantitatively recovered by heating the PBX at 160°C for 10 to 15 hr and then dissolving the decomposed binder with methylene chloride.

General Approach

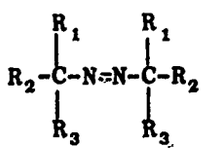
In the current program we prepared difunctional azo compounds in order to identify a heat-sensitive compound that will be suitable for use in RDX-loaded PBXs. One of two basic criteria for a heat-sensitive binder for use with RDX is decomposition at 130 to 140°C in 0.5 to 2 hr, so that the binder can be readily decomposed with minimum decomposition of the explosive ingredient. The other is that decomposition must be minimal under the most severe storage conditions, as judged by such surveillance tests as the vacuum stability tests, generally at 100°C, and the WR-50 thermal cycling test, where the maximum temperature is 71°C.

The relation between binder stability and the effect of the heat-sensitive group depends on the degree of decomposition of the

heat-sensitive groups and the relative amounts of heat-sensitive groups and crosslinks in the polymer. A crosslinked binder will begin to significantly lose its physical properties when the number of polymer chain cleavages equals one-half the number of crosslinks. At this point the crosslinked structure would be reduced to a linear structure of high molecular weight. Further cleavage would reduce the average molecular weight of the linear fragments. A total of one induced cleavage per initial crosslink reduces the average molecular weight to a value corresponding to the initial molecular weight per crosslink (generally 2000 to 4000 for crosslinked polyurethanes). These properties cause the polymer to change from a resilient material to a viscous fluid and from an insoluble material to one readily soluble in common organic solvents. For the desired amount of polymer cleavage, a crosslinked binder must have about one heat-sensitive group per crosslink. This will cause the crosslinked polymer to be reduced to a linear polymer under the time-temperature conditions where one-half of the group are decomposed (one half-life). After a second half-life (75% decomposition), the molecular weight of the decomposed polymer will approach that of the units between crosslinks.

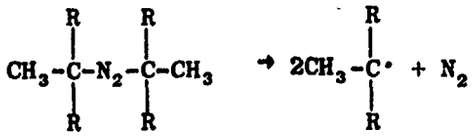
Previous Work

Earlier[2], we demonstrated that it is practical to use substituted azo compounds (I) as heat-sensitive groups.

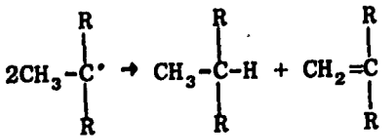


(I)

The decomposition rate of the azo group is affected by the size of the alkyl substituent (R_1, R_2, and R_3), and thus, it can be adjusted by altering the substituents. The decomposition reaction is

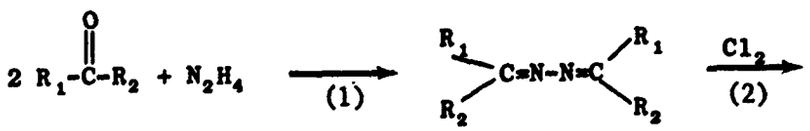


where the radical product disproportionates.

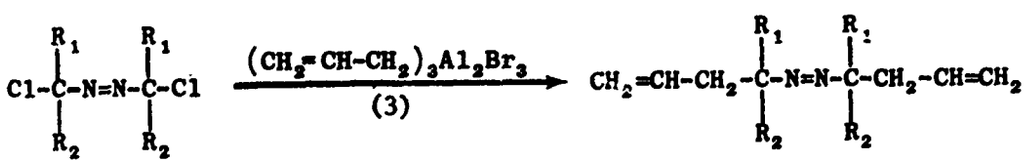


Thus, if the azo group is chemically bonded into a main chain of the binder, decomposition of the azo compound will result in cleavage of the polymer chain. We have found that azo compounds can be readily incorporated into the binder if an alcohol function is incorporated on each side of azo linkage, that is, if the azo compound is an azodiol. Thus, the azodiol may be used as a typical diol in conventional urethane binders.

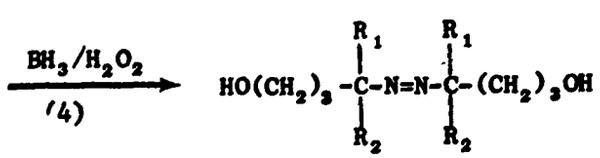
The general synthetic approach developed during Phase I of the current contract and used to prepare azodiols was as follows:[3]



azine



azodiene



azodiol

Many examples are known where reactions similar to steps (1), (2), and (4) proceed in good yields. Reactions analogous to (3) were not documented previously but the suitability of this step was demonstrated in Phase I.

RESULTS AND DISCUSSION

Decomposition of BPTA in Solution

The decomposition of BPTA was investigated using polypropylene glycol with a molecular weight of 2010 (PPG-2010) as the solvent. This material has very low volatility and a reactivity to free radical attack no greater than that of polyglycol materials used in polyurethane binder formulations. Decompositions were first done at 140° and 200°C to determine the yield of nitrogen and then at 100, 120, and 140°C to determine the rates of decomposition. These results are summarized in Table 1.

The yields of total nitrogen evolved at 100, 140, and 200°C are 107, 95, and 104% of theoretical, respectively, which we believe are within experimental error of the 100% value expected. Thus, the incomplete evolution of nitrogen reported earlier[3] when chloroform was used as a solvent do not occur with the PPG solvent. The problem in chloroform may be due to free radical attack on decomposed BPTA (RN=NR). We believe the reactions are

$$RN{-}NR \rightarrow N_2 + 2R\cdot$$

$$R\cdot + HCCl_3 \rightarrow RCl + HCCl_2\cdot$$

$$HCCl_2\cdot + RN{=}NR \rightarrow HCCl_2\overset{R}{\underset{\cdot}{N}}NR$$

Although the above type of reactions are not reported in the decomposition of most azo compounds studied, there are a limited number of cases where these reactions have been proposed.[4] According to the above mechanism, as the concentration of azo compounds is decreased, the incomplete evolution of nitrogen should become less important because of the dual participation of the azo compound in the process. The reactivity of the solvent is also an important factor and we believe it to be the major source of the problem in this case. The kinetic runs at 100 to 140°C in PPG-2010 all give good first-order decays, as judged

Table 1

DECOMPOSITION OF BPTA IN PPG-2010 SOLUTION

Temperature (°C)	Time (hr)	BPTA (10^5 mol)	Nitrogen (10^5 mol)	Nitrogen Percent	CO[a] (%)	10^6 k_D (s^{-1})
100	22.0	7.88	1.85	23.4	2.16	3.36
	47.6	7.44	3.63	48.8	6.45	3.91
	64.3	8.39	4.80	57.2	6.55	3.67
	75.0	9.90	6.15	62.4	9.70	3.62
	100.0	8.64	6.32	73.1	14.4	3.65
	478	7.16	7.68	107	28.0	-
120	2.0	8.42	1.40	16.6	1.78	25.2
	3.0	9.67	3.33	34.8	4.55	39.6
	4.0	8.85	3.87	43.7	3.28	39.8
	5.5	10.23	5.16	50.4	4.49	35.4
	8.5	10.48	7.36	70.2	8.3	39.6
	10.16	5.08	3.95	77.8	15.0	41.1
140	0.25	8.52	1.99	23.4	1.90	296
	0.33	9.59	3.47	36.2	2.39	378
	0.50	8.44	4.30	50.9	2.72	395
	0.75	5.98	3.75	62.7	5.18	365
	1.00	7.56	5.67	75.0	7.36	385
	20.0	7.81	7.41	94.8	8.2	-
200	2.0	11.06	11.54	104	14.0	-

[a]Based on moles of BPTA.

by small variations with time in the calculated first-order rate constants. This further supports the lack of any secondary reactions affecting the decomposition. Thus, the effects we have seen previously are the result of reactions with the solvent. In our experiment, PPG-2010, which is structurally similar to the types of materials that make up the major part of most polyurethane binders, does not undergo this type of reaction; therefore, the reaction should be unimportant in the final binder.

The data in Table 1 also show that carbon monoxide is formed in the BPTA decompositions. The amounts range from 10 to 25% of the decomposed BPTA with little variation over the entire temperature range. We believe this effect is due to the reaction of the alcohol functions in the BPTA ($R'CH_2OH$) by the radicals ($R\cdot$) that are formed, followed by a free radical decarbonylation. The suggested reactions are

$$2R\cdot + R'CH_2OH \rightarrow 2RH + R'CHO$$
$$R\cdot + R'CHO \rightarrow RH + R'\dot{C}O$$
$$R'\dot{C}O \rightarrow R'\cdot + CO$$

This complication should not be important in a binder because the alcohol groups are eliminated during the formation of the binder.

Decomposition of BPTA Chemically Bonded in a Polymer

BPTA was incorporated into a polyurethane using the following formulation: 1.0 mmol BPTA, 1.5 mmol PPB-2010, 0.5 mmol trimethylol propane, and 3.25 mmole toluene diisocyanate. The polymer was very flexible and resilient, although slightly tacky. Samples of the polymer were decomposed to determine the rate of decomposition of BPTA in the polymer and to determine the total available nitrogen released upon extensive decomposition. The results are summarized in Table 2.

Table 2

DECOMPOSITION OF BPTA IN A POLYURETHANE POLYMER

Temperature (°C)	Time (hr)	BPTA (10^5 mol)	Nitrogen (10^5 mol)	Nitrogen Percent	10^6 k_D (s^{-1})
100	22.83	10.57	2.58	24.4	3.40
	4[illegible]31	8.79	3.74	42.5	3.38
	75[illegible]	9.93	5.52	55.6	3.01
	93.0	7.04	4.50	63.9	3.04
	101.4	11.28	7.63	67.6	3.09
	450	7.65	7.26	94.9	-
120	2.0	11.76	2.97	25.3	40.5
	3.0	13.12	4.30	32.8	36.8
	4.5	10.87	4.38	40.3	31.8
	8.0	12.07	7.6	63.0	34.5
	10.0	9.12	6.65	72.9	36.3
140	0.25	9.25	2.59	28.0	365.0
	0.33	11.43	4.03	35.3	367.0
	0.50	8.47	4.14	49.0	374.0
	0.87	8.11	5.53	68.2	366.0
	1.0	7.25	5.24	72.2	356.0
	2.0	12.1	10.73	88.7	303.0
	18.25	10.32	8.89	85.6	-
200	2.0	12.10	10.73	88.7	-

The nitrogen generated by totally decomposing the BPTA polymer at 100, 140, and 200°C accounted for 54.9, 85.6, and 88.7% of the expected amount, respectively. These values agree well with the nitrogen yields obtained with a sample prepared similarly and reported in the last report. Because of the small amount of BPTA used in the formulation, the low nitrogen yield could reflect inaccuracies associated with weighing the BPTA; however, it seems unlikely that both samples should give good agreement if the error was random. The discrepancy is not strongly temperature-dependent, and although the cause of the low nitrogen yield is not clear, it does not appear that it would present any problem later in the development. For the kinetic study, we have used the amount of BPTA indicated by the total nitrogen evolution.

The decompositions reported in Table 2 show very good first-order kinetics. The rate constants obtained at each temperature are in excellent agreement with those obtained from the decomposition of BPTA in PPG solution. This agreement verifies one of the basic assumptions used in the development of this program, namely, that the unimolecular decomposition will occur at the same rate in either a solution or a polymer matrix.

The solubilities of the partially decomposed polymer samples were tested in methylene chloride. At each temperature, the polymer became soluble at the point where the amount of decomposed BPTA equalled one-half of the number of crosslinking groups in the polymer. This degree of decomposition, predicted by the basic theory, corresponds to the point where the crosslinked polymer of infinite molecular weight has been converted to a linear polymer of relatively high molecular weight.

Preparation of Model Binders

A series of five binder formulations was prepared to probe the effects of cross-link density, mole fraction BPTA, and chemical composition of the formulation on binder and PBX behavior. Compositions and some characteristics of the binders are summarized in Table 3.

Table 3

BINDER FORMULATIONS AND CHARACTERISTICS

Designation	Component	(mmol)[a]	Molecular Weight per Crosslink	Mol BPTA per Mol crosslink	Mol N_2 evolved per Mol BPTA	BPTA (wt %)
SRI-1	BPTA (2)	PPG (6)		1	1.06	4.9
	TMP (2)	TDI (15)	8,300			
	HD (4)					
SRI-2	BPTA (3)	PPG (6)		1.5	1.14	7.2
	TMP (2)	TDI (15)	8,300			
	HD (3)					
SRI-3	BPTA (4)	PPG (6)		2	1.11	9.5
	TMP (2)	TDI (15)	8,300			
	HD (2)					
SRI-4	BPTA (0)	PPG (6)				
	TMP (2)	TDI (15)	8,300	0	[c]	0
	HD (6)					
SRI-5	BPTA (17)	L-35 (50)	12,500	1	0.95	3.2
	TPE (17)	Hylene W (100)				

[a] Abbreviations used: BPTA [1,1'-bis(3-hydroxypropyl)-1,1',1'-tetraisobutyl azomethane], TMP (trimethylol propane), HD (1,6-hexanediol), PPG [2010 molecular weight poly(propylene glycol)], TDI (1,3-toluene diisocyanate), TPE 4542 polyethylene oxide end-capped TMP), L-35 (50/50 ethylene oxide/propylene oxide hydroxy-terminated co-polymer), Hylene W [methylene bis-(4-cyclohexyl)isocyanate].

[b] Determined by measuring N_2 evolved from sample of binder heated 20 hr at 140°C.

[c] 2×10^{-2} mole N_2 evolved per gram of binder.

Details of the preparations are given in the Experimental Procedures section. Binders SRI-1 through SRI-4 all comprised the following:

PPG-2010	Poly(propylene glycol) mw 2010
HD	1,6-Hexanediol
BPTA	1,1-bis(3-hydroxypropyl)-1,1,1',1'-tetraisobutyl azomethane
TMP	Trimethylol propane
TDI	Toluene diisocyanate

In the formulations, the molecular weight per crosslink (MW/XL) ratio was maintained at a constant value, but the BPTA ratio was varied.

Binder SRI-5 comprised the following:

L-35	50/50 Ethylene oxide/propylene oxide hydroxy-terminated co-polymer
BPTA	1,1-bis(3-hydroxypropyl)-1,1,1',1'-tetraisobutyl azomethane
TPE-4542	(a chain-extended TMP)
Hylene W	Methylene bis-(4-cyclohexylisocyanate)

In this formulation the MW/XL ratio was higher than in binders SRI-1 through -4, although the BPTA/XL ratio was the same as in binder SRI-1.

All five binders were resilient and flexible, though slightly tacky. All were swollen by CH_2Cl_2, indicating that they were highly crosslinked On heating overnight for 140°C, four of the binders evolved (within experimental uncertainty) the theoretical amount of N_2 based on the weight percent of BPTA in the formulations. The exception was binder SRI-4, which contained no BPTA and which evolved only trace amounts of N_2. These data are consistent with our earlier observation[4] that BPTA decomposition proceeds quantitatively for BPTA bound to a polymer matrix.

Molecular Weight Reduction of Model Binders

We had previously noted that polyurethanes containing BPTA as a heat-sensitive group are transformed from insoluble to soluble materials by heating 30 min at 140°C. Though this is a meaningful observation, it is desirable to understand more quantitatively how degradation of the binder is affected by the BPTA/XL and MW/XL ratios, and by the time and temperature of decomposition. Detailed knowledge of the reduction in binder molecular weight as a function of these variables would permit selection of an optimum binder formulation with respect to the minimum amount of azo diol required to effect rapid degradation of the binder into low-molecular-weight (soluble) material.

We have pursued this line of investigation with the series of binders listed in Table 3. Samples of approximately 100 mg of each binder were placed in sealed tubes under an argon atmosphere and were heated for timed intervals at 140°C. Each sample was then dissolved in 10 ml of tetrahydrofuran (THF), and the molecular weight distribution was determined by gel permeation chromatography (GPC; see Experimental Procedures). For each sample, the distribution was expressed as a number average molecular weight, M_N, where:

$$M_N = \frac{\sum_{i}^{n} N_i M_i}{\sum_{i} N_i}$$

and where N_i = number of molecules of $\underline{i}$th molecular weight and M_i = $\underline{i}$th molecular weight.

The molecular weight distributions were calibrated using polystyrene standards of known molecular weight. Because hydrogen bonding and similar chemical effects can alter the chromatographic behavior of high molecular weight species, the actual molecular weight distributions for the polyurethane binders differ significantly from those calculated on the basis of the polystyrene standards. Therefore, values of M_N determined by this method do not necessarily give an absolute measure of the molecular

weight distribution. However, such M_N values are sufficient to accurately describe relative changes in molecular weight for a series of chemically similar species.

Results of the GPC studies are presented in Table 4. The table shows that for each binder, M_N values decreases with time and that the molecular weight reduction is accompanied by transformation of the polymer into a THF-soluble material. This behavior is best understood in terms of the BPTA decomposed/XL ratio--that is, the ratio of the number of cleavages between polymer chains per crosslink. This ratio is given by the following equation:

$$\frac{\text{BPTA decomposed}}{\text{XL}} = \left\{\frac{\text{mole BPTA}}{\text{mole XL}}\right\}_{\text{initial}} \{1 - \exp[-kt]\}$$

where k = rate constant for BPTA decomposition
= 2.23×10^{-3} min^{-1} at 140^{o},
and t = decomposition time.

Understandably, M_N decreases with increasing BPTA Decomposed/XL, inasmuch as there are an increasing number of breaks between polymer chains. From the above equation, M_N will also decrease with increasing initial (mol BPTA)/(mol XL) ratio. Thus, at a given decomposition time, M_N will be smaller for binders with higher initial (mol BPTA)/(mol XL) ratios. This is clearly seen in Table 2 for the series of binders SRI-1, -2, and -3. These binders have initial (mol BPTA)/(mol XL) ratios of 1, 1.5, and 2, respectively, and after a 15-min decomposition period, the corresponding M_N values are 89×10^3, 38×10^3, and $22 \times 22 \times 10^3$. At long decomposition times, the BPTA decomposed/XL values approach a maximum value equal to the initial (mol BPTA)/(mol XL) ratio. For this reason, M_N values asymptotically approach a minimum at long reaction times. This type of behavior is best demonstrated by binder SRI-1, which yields constant M_N = 10 to 11 $\times 10^3$ at decomposition times exceeding approximately 60 min.

Table 4

NUMBER AVERAGE MOLECULAR WEIGHT DISTRIBUTION (M_N) OF BINDERS DEGRADED AT 140°C[a]

Binder[b,c]	SRI-1		SRI-2		SR-3		SRI-5	
Time (Min)	BPTA Decomp per XL	M_N x 10^{-3}	BPTA Decomp per XL	M_N x 10^{-3}	BPTA Decomp per XL	M_N x 10^{-3}	BPTA Decomp per XL	M_N x 10^{-3}
10	--	--	0.25	88	0.35	53	--	--
15	0.28	89	0.43	38[d]	0.57	22[d]	0.29	233
30	0.49	26[d]	0.73	11	0.98	19	0.49	182[d]
45	0.63	13	0.89	12	1.3	10	0.63	60
60	0.74	10	1.1	9.2	--	--	0.75	49
90	0.90	11	--	--	--	--	0.90	50
120	0.93	11	--	--	1.9	9.0	0.93	33

[a] BPTA Decomp/per XL ratio is determined from equation in text.
[b] See Table 3 for binder formulations.
[c] Binder SRI-4 was omitted since no solubilization was obtained on heating.
[d] Approximate point at which binder becomes completely soluble in THF.

Another important factor is the initial MW/XL ratio. Clearly, for a given BPTA Decomposed/XL ratio, M_N values will be higher for binders having higher initial MW/XL. Comparing binders SRI-2 and -5, for example, shows that at all values of BPTA Decomposed/XL, SRI-5 (initial MW/XL = 12500) exhibits higher values of M_N than does SRI-1 (initial MW/XL = 8300).

A final point concerns the factors governing the conditions required to transform a crosslinked binder into soluble material. As noted in the Introduction, the conversion from a crosslinked to linear (soluble) polymer should occur when the number of cleavages between polymer chains is equal to one-half the initial crosslinks, that is, when BPTA Decomposed/XL = 0.5. Table 4 shows that the data conform in general to this expectation and that the point of solubilization is independent of initial MW/XL (compare binders SRI-1 and -5). Thus, we conclude that we can reliably predict the time required to achieve solubilization (or any degree of degradation) for any of a variety of binders given only the degradation temperature, the initial (mol BPTA)/mol XL) ratio, and the rate constant for BPTA decomposition at the temperature in question.

Model PBX Preparation and Degradation

Binder SRI-5 and a trimodal (22% fine, 32% medium, 46% coarse) particle distribution of RDX were used to prepare a model PBX (BPTA-PBX-1). The composition of the PBX was 20% binder and 80% RDX. Agitation of samples of the PBX in CH_2Cl_2 did not separate RDX from the binder.

A cursory examination was made of the feasibility of recovering RDX from the PBX following thermal degradation of the binder. Two 150-mg samples of the PBX were sealed in tubes under argon and heated 60 min at 140°C. Then 10 ml of solvent was added to each tube. The mixtures were agitated with a spatula and vacuum filtered. The filtrate (a white, granular solid) was recovered and weighed, and the percent recovery was determined based on the amount of RDX in the initial samples. CH_2Cl_2 and CCl_4 were used as solvents, and recoveries were 63 and 79%, respectively. That the recoveries were well below 100% is attributable to partial solubility of RDX in the solvents and loss of the fine particles

of the RDX mix in the rather coarse (Whatman No. 1) filter paper used. Proper choice of solvent and filtration method would likely increase the percent recovery, and this line of investigation needs to be pursued further. However, our preliminary data definitely show that efficient recovery of RDX from a thermally degraded PBX is feasible.

To determine what solvents may be used to dissolve the decomposed binder, we have checked the solubility of a decomposed binder (SRI-2) in a number of solvents. The following solvents readily dissolved the degraded binder: carbon tetrachloride, methylene chloride, tetrahydrofuran, ethyl acetate, benzene, and cellosolve acetate. The decomposed binder did not dissolve in hexane. Thus, the results indicate that polar organic solvents generally are good solvents for the degraded binder. The solvent or mixed solvent of choice will dissolve RDX to a minimum degree while totally dissolving the binder.

Compatibility of BPTA in Model PBX Formulation

To demonstrate that incorporation of BPTA in a PBX formulation has no significant effect on the formulation other than to render the binder thermally degradable, we performed a series of vacuum thermal stability (VTS) and differential scanning calorimetry (DSC) tests.

First, VTS tests were carried out on SRI-1, PBX(BPTA-PBX-1), and pure RDX;[5] in all cases the gas evolution was less than 1 cc/g, indicating no significant decomposition.

DSC was performed on the pure trimodel RDX mix; RDX recovered from degraded PBX; binders SRI-1, -4, and -5; and BPTA. Onset temperatures for each system exhibiting endotherm (indicative of a phase change such as melting) and/or exotherm (indicative of decomposition) were determined. These data are summarized in Table 5.

Table 5

ONSET TEMPERATURES FOR ENDOTHERM (T_{endo}) AND EXOTHERM (T_{exo}) FOR RDX, PBX, VARIOUS BINDERS, AND BPTA BY DIFFERENTIAL SCANNING CALORIMETRY

System	T_{endo} (K)	T_{exo} (K)
Trimodal RDX	462.6	485.6
RDX recovered from BPTA-BPX-1	461.8	485.3
BPTA-PBX-1	460.0	481.3
SRI-1	a	a
SRI-4	a	a
SRI-5	a	a
BPTA	a	422.5

[a]Not detectable.

Table 5 shows that the temperature for onset of endotherm (T_{endo}) for pure RDX is only 0.8 K higher than for RDX recovered from degraded PBX. This is a good indication that the recovered RDX is pure, because significant amounts of impurities in the recovered RDX would have resulted in a large melting point depression and concommitant reduction in T_{endo}. The PBX itself exhibits a T_{endo} that is 2.6 K lower than that of RDX. Such a difference is not surprising inasmuch as the RDX is incorporated into a polymer matrix in the PBX.

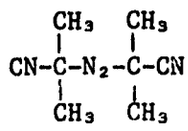
A more meaningful parameter with respect to the model PBX is the temperature for onset of exotherm (T_{exo}). T_{exo} for the PBX is only 4.3 K lower than T_{exo} for pure RDX. This demonstrates that incorporation of RDX into a binder containing BPTA does not confer an unusual temperature sensitivity to the RDX. This is to be expected, because the SRI-5 binder (which constitutes only 20% of the PBX) contains only 3.2 wt% of BPTA.

To obtain another indication that BPTA is compatible with the PBX formulation, we have analyzed quantitatively the exothermic behavior of BPTA-PBX-1 in terms of the activation energy (E_a) for decomposition of the RDX. As described by Rogers and Morris,[5] a plot of log(rate of heat evolution) versus 1/T for an exothermic reaction should yield a straight line with slope = $E_a/4.58$. For BPTA-PBX-1, such a plot (not shown) is linear over a large temperature range and yields a value of E_a = 46.9 kcal/mol. This value compares very favorably with the value of E_a = 48.4 reported by Rogers and Morris for decomposition of pure RDX in polyphenyl ether solvent. Again, the small difference in activation energies between the PBX and RDX is an indication of the compatibility of BPTA in the PBX formulation.

Toxicity of BPTA

Because BPTA is a new compound, no data exist on its toxicity; however, examination of other aliphatic compounds containing the azo function suggests no significant toxicity problem. For example, azoethane ($CH_3CH_2N_2CH_2CH_3$) is reported[7] to have TCL_o (lowest published toxic concentration) of 4800 ppm for 1 hr in inhalation experiments with rats. Teratogenic effects were observed at this level, but the concentrations are extreme and correspond to 0.48% of the air.

A second azo compound for which there is data is 2,2'-azobis (2-methylpropanenitrite),[7]



Oral tests with mice give LD_{50} values of 100 mg/kg; intraperitoneal tests on mice give LD_{50} values of 25 mg/kg.

From these comparisons, there does not appear to be any reason to expect BPTA to be unusually toxic. Furthermore, the high molecular weight of BPTA suggests that the boiling point is in excess of 300°C and the vapor pressure at room temperature is well below 1 ppm. Thus, the possibility of inhaling significant amounts is very low.

EXPERIMENTAL PROCEDURES

Kinetic Measurements

Rates of decomposition of BPTA in PPG-2010 solvent and in cross-linked polymer were determined by gas evolution. Samples were accurately weighed into breakseal flasks; degassed by four freeze-pump-thaw cycles; sealed; and heated at 100, 120, or 140°C for timed intervals. A calibrated gas burette was used to measure the amount of gas evolved from each sample. For the gas analysis, samples were cooled to -196°C so that only noncondensable gases were measured. Mass spectral analysis indicated the total gas evolved to be primarily N_2 with varying amounts of CO. The amount of CO present in each sample was quantitated by passing the total gas evolved through a CuO furnace and a -196°C trap. This procedure converted any CO to CO_2, the latter being condensed at -196°C. The remaining gas (N_2) was measured on the gas burette; the amount of CO present was determined by subtracting the amount of N_2 from the value for the total gas. The rate constants for decomposition for each sample were determined from the expression:

$$k_D = \frac{1}{t} \ln[1-(\text{mols } N_2 \text{ evolved/initial mols BPTA})]$$

Polymer Preparation

SRI-1

A mixture of 2 mmol BPTA (0.79 g), 6 mmol PPG_{2010} (12 g), 2 mmol TMP (0.27 g), and 3 mmol HD (0.36 g) was heated in bulk under nitrogen at 65°C for 15 min. The resulting clear mix was cooled to room temperature, and 15 mmols TDI (2.61 g) was added. After mixing for 5 min, the solution was discharged onto a shallow dish and the uncured binder was degassed, and the cured overnight at 35°C under nitrogen.

Abbreviations used: BPTA [1,1'-bis(3-hydroxypropyl)-1,1,1',1'-tetra-isobutyl azomethane], PPG_{2010} [polylproplene glycol, MW 2000], TMP [trimethylylol propane], HD [hexane diol], TDI [80/20 toluene diisocyanate]; 0.1% dibutyl tin dilaurate used as a catalyst in all polymers.

SRI-2

A mixture of 3 mmol BPTA (1.19 g), 6 mmol PPG_{2010} (12 g), 2 mmol TMP (0.27 g), and 3 mmol HD (0.36 g) was heated in bulk under nitrogen at 65°C for 15 min. The resulting clear mix was cooled to room temperature, and 15 mmol TDI (2.61 g) was added. After mixing for 5 min, the solution was discharged onto a shallow dish and the uncured binder was degassed, and then cured overnight at 35°C under nitrogen.

SRI-3

A mixture of 4 mmol BPTA (1.58 g), 6 mmol PPG_{2010} (12 g), 2 mmol TMP (0.27 g), and 2 mmol HD (0.24 g) was heated in bulk under nitrogen at 65°C for 15 min. The resulting clear mix was cooled to room temperature, and 15 mmol TDI (2.61 g) was added. After mixing for 5 min, the solution was discharged onto a shallow dish, and the undured bunder was degassed, and then curred overnight at 35°C under nitrogen.

SRI-4

A mixture of 6 mmol PPG_{2010} (12 g), 2 mmol TMP (0.27 g), and 6mmol HD (0.72 g) was heated in bulk under nitrogen at 65°C for 15 min. The resulting clear mix was cooled to room temperature, and 100 mmol Hylene W (26.5 g) was added. After mixing for 5 min, the solution was discharged onto a shallow dish, and the uncured binder was degassed, and then cured at 70°C for 16 hr under nitrogen.

BPTA-PBX-1

A mixture of 1.25 g of SRI-5 binder and 5 g of trimodal RDX (22% fine, 32% medium, 46% coarse) was degassed and cured for 16 hr at 70°C under nitrogen.

Side Compound Synthesis

Diisobutyl Ketazine

A solution of 50 g (0.35 mol) diisobutyl ketone and 5.12 g (0.16 mol) 99% hydrazine was heated to 100°C for 24 hr. To the cooled solution was added an equal volume of diethyl ether, and the aqueous phase was removed. The ether solution was dried over $MgSO_4$ and the solvent was evaporated.

The resulting liquid was distilled under vacuum through a 12-inch vigreux column. The fraction boiling at 106°C (1 mm) was collected and represented a 73% yield of the required product.

1,1'-Dichloro-1,1,1',1'-tetraisobutyl Azomethane

Diisobutyl ketazine (10 g 0.036 mol) was dissolved in 100 ml dichloromethane and cooled to -78°C in a dry ice-acetone bath. This system was placed in total darkness, and a slow stream of chlorine gas was introduced into the solution for 1 hr while the reaction temperature was maintained at less than -60°C. The mixture was allowed to react for 2 hr and then to warm to room temperature. Removal of the solvent yielded a pale-yellow oil, which, on repeated recrystallization from petroleum ether, yielded a white solid that melted at room temperature (lit mp 30°C). Analyses by nmr and ir were consistent with the assigned structure. Analysis by uv in hexane gave λ_{max} at 358 nm, ε = 20.8, which agrees with published data.

1,1'-Diallyl-1,1,1',1'-tetraisobutyl Azomethane

Allyl aluminum sesquibromide was prepared by refluxing a mixture of 7.83 g (0.29 g-atom) aluminum with 52.8 g (0.44 mol) allyl bromide in 500 ml diethyl ether with 200 mg mercuric chloride catalyst for 24 hr.

The resulting dark solution was diluted with 1000 ml diethyl ether and then cooled to -10°C. To this solution was added 19.11 g (0.053 mol) 1,1'-dichloro-1,1,1',1'-tetrabutyl azomethane in 300 ml diethyl ether dropwise over a 90-min period while the reaction temperature was maintained at -10°C. After complete addition, the resulting solution was further reacted for 4 hr at -10°C and then allowed to warm to room temperature

overnight and then hydrolyzed with 100 ml saturated aqueous ammonium chloride solution with cooling (∿10°C).

The organic layer was removed, dried over $MgSO_4$, and evaporated to constant weight at room temperature. The resulting oil was purified by passing it through a silica gel column and eluting with hexane. Removal of the solvent yielded 11.8 g (60%) of a bright-yellow mobile oil. Nmr and ir analyses were consistent with the assigned structure. Uv analysis in hexane gave λ_{max} = 387, ε = 25.1.

Elemental analysis for $C_{24}H_{46}N_2$: Calc: C, 79.56; H, 12.71; N, 7.74
Found: C, 79.42; H, 13.31; N, 7.72

1,1'-(3-Hydroxypropyl)-1,1,1',1'-tetraisobutyl Azomethane

In 60 ml dry THF was dissolved 11 g (0.03 mol) 1,1'-allyl-1,1,1',1'-tetraisobutyl azomethane, and the solution was cooled to -5°C. To this solution, 33 ml 1M BH_3·THF in THF was added in 0.5-ml portions over a 30-min period while the reaction temperature was maintained at -5°C. After complete addition, the reaction temperature was maintained at -5°C for an additional 2 hr.

To this solution at 0°C was added slowly a solution containing 4.4 g NaOH and 12.1 g 30% H_2O_2 in 50 ml of water. The resulting mixture was allowed to warm to room temperature and react for an additional 2 hr. The solution was then extracted with diethyl ether, and the extract was dried over $MgSO_4$ and evaporated to constant weight at room temperature. This product was passed down a silica gel column and eluted with chloroform. The product was eluted with a 10:90 mixture of methyl alcohol and chloroform. The solvent was evaporated to yield 7.1 g (59%) of a white waxy solid that melted at about 32°C. Analyses by nmr and ir gave results consistent with the required structure. Analysis by uv in hexane gave λ_{max} = 385, ε = 24.6.

Elemental analysis for $C_{24}H_{50}N_2O_2$: Calc: C, 72.4; H, 12.6; N, 7.04
Found: C, 73.61; H, 13.8; N, 7.15

Gel Permeation Chromatography (GPC)

Four μ-Styragel columns (pore sizes 10^6, 10^5, 10^4, 10^3 Å) in series were used for GPC determinations. THF was used as a mobile phase for GPC (flow rate = 1.0 ml/min) and as a solvent for the degraded binders. A solution of polystyrene standards of known molecular weight (ranging from 800 to 2×10^6 g/mole) was used to calibrate the GPC in terms of molecular weight versus retention volume. Molecular weight distributions for degraded binders were determined by obtaining GPC curves for the binders and measuring peak heights at 10 to 15 points along the curve. Because peak heights are proportional to concentration and retention volumes are proportional to molecular weight, data so obtained could be used to calculate number average molecular weights (See Results and Discussion section).

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer model 1B DSC was used for all determinations. Samples (1 to 10 mg) were accurately weighted into aluminum pans and covered with aluminum lids. An empty, covered pan was used as a reference in all runs. The rate of heat adsorption or evolution (normalized on a mcal/mg-s basis) was measured as a function of temperature over the range 300 to 500 K, using a 10 K/min scanning rate. A tin standard ($m.;. = 503.6$ K) was used to calibrate the temperature scale of the instrument.

TECHNICAL FORECAST

Problem

Explosive ordnance, rocket motors, and pyrotechnics have a limited storage lifetime and require disposal after the safe operational period has passed. Disposal methods have consisted of dumping at sea, burning, or other means not involving recycling or environmentally acceptable procedures. However, dumping of explosive compositions is now severely restricted and, in addition, calculations indicate that it is uneconomic. Moreover, in 1972, Indiana imposed a total ban on the disposal of explosives by open burning. Many other states have followed suit with similar restrictions.

Current methods of demilitarization of ordnance include removal of the charge or propellant by solvent extraction, melting, and hydraulic cutting of soft compositions. However, the components still must be recycled or disposed. Thus, the real problem of environmentally acceptable ordnance disposal is only partly resolved by current practices. For the long-term future, significant improvements in several areas of ordnance disposal must be made.

Two approaches are being investigated to achieve effective and environmentally acceptable disposal methods: (1) maintain current formulation processes and dispose of obsolete ordnance by mechanical removal followed by controlled burning or recycling, and (2) in future ordnance, use ingredients that allow control of degradation by simple chemical or physical means. Approach (1) is simply ar extension of the state of the art, which is not always applicable. Approach (2) is much longer range and requires the development of new formulations that will meet all operational specifications and at the same time incorporate the properties necessary to facilitate removal and disposal of ordnance.

Modification of the binder ingredients in an explosive or propellant formulation appears to be the best and quickest means of facilitating disposa disposal. Because the binder is present in relatively low concentration (for example, usually 5-15 wt % in a PBX), only a relatively small quantity of degraded material needs to be handled during the recovery and recycle of explosives. Moreover, because this relatively small fraction of the binder determines the physical properties of the composition, its modification can have the greatest effect on the physical properties. Thus, we have concentrated on : (1) establishing the binder characteristics that would make the ingredients vulnerable to disposal methods and yet still meet operational requirements, and (2) applying the results of the characteristics study to develop a practical system, and (3) making a preliminary test of the system's feasibility. Experimentally, we have dealt with the problem of how best to synthesize thermally degradable polymers for use in explosive formulations to improve disposal characteristics without loss in the overall performance. Then we conducted feasibility tests.

The concepts and polymers developed in this program will have potential application to other Navy requirements, such as improved formulations for disposal of propellants, as well as to explosives and propellants used by the ARmy and Air Force.

State of Technology and Forecast

Before this program began, most of the work on disposal of ordnance was concerned with dumping, destruction, and recycling of standard compositions.In an earlier program, we evaluated several approaches for achieving easy disposal. Only the use of thermally degradable binders appeared to us to be potentially nonpolluting and economical as required for for ordnance disposal. The azo groups appeared most useful for heat-sensitive links in polymers.

During the previous program,[2] a crosslinked, heat-sensitive polyurethane similar to those used in conventional PBX systems was obtained by bulk polymerization. When this polyurethane was subsequently loaded to 85 wt% with HMX, we obtained a white rubbery PBX. When degraded at elevated temperatures, the PBX lost all rigid properties and gave a

paste that could easily be moved mechanically. The degraded polymer was soluble in common organic solvents, and all the HMX was recovered unchanged.

We have now developed a heat-sensitive structure that is suitable for use in polyurethane formulations containing RDX. Formulations containing this structure show good physical properties and no complications associated with incompatability. Data indicate long-term stability of the structure at ambient conditions. However, when the binder is heated to the appropriate elevated temperatures, it decomposes, allowing the formulations to be removed from an ordnance and the RDX to be recycled.

On the basis of the work completed during this contract, an entirely new method of facilitating ordnance disposal has been defined and evaluated. Figure 1 shows a schematic estimate of the probable future of various methods of ordnance disposal.

Suggestions and Implications

Because of the increased interest in pollution abatement, environmental restrictions on disposal of ordnance are expected to become more stringent. Under this contract, we have successfully demonstrated the use of a heat-sensitive polymer to facilitate disposal of PBXs containing RDX. The next step in this development is to conduct the tests necessary for interim qualifications of a formulation having the heat-sensitive structure that has been identified.

In summary, the usefulness of the heat-sensitive binder approach to ordnance disposal depends on many interrelated factors and their effects on physical and chemical properties. However, we have identified an azo group that gives the desired heat sensitivity and have demonstrated laboratory feasibility of the system. If polymers containing the identified azo group continue performing in explosive formulations as well as has been observed, then the thermally degradable binder approach will provide a practical means of facilitating future ordnance disposal.

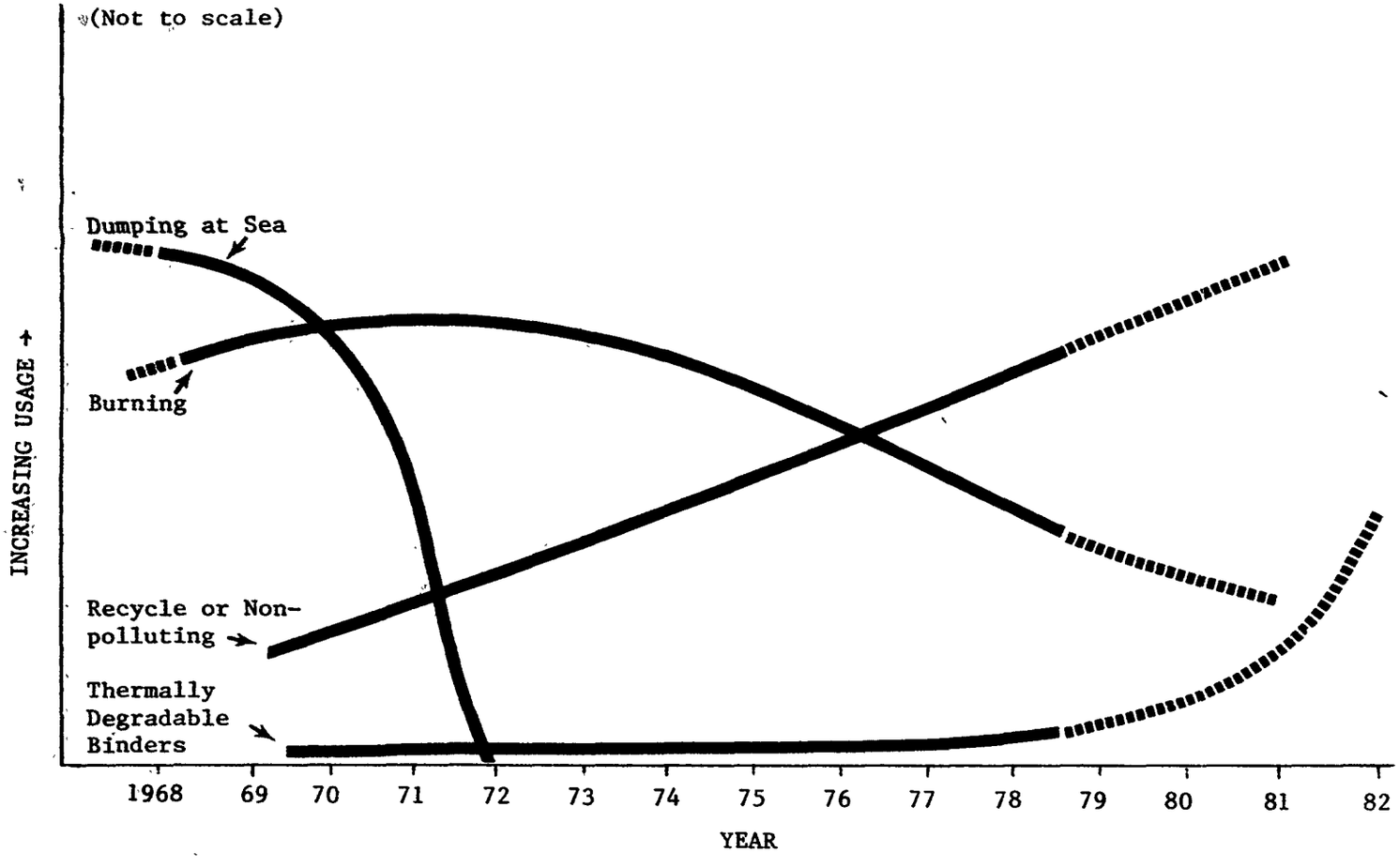


FIGURE 1. TECHNICAL FORECAST FOR ORDNANCE DISPOSAL METHODS

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